WORLD INTELLECTUAL PROPERTY ORGAN International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classificati n 5:

C08K 3/34, C08L 23/00

(11) International Publication Number:

WO 92/13029

A1

(43) International Publication Date:

6 August 1992 (06.08.92)

(21) International Application Number:

PCT/SE92/00029

(22) International Filing Date:

20 January 1992 (20.01.92)

(30) Priority data:

9100181-8

22 January 1991 (22.01.91) SE

(71) Applicant (for all designated States except US): NESTE OY

(72) Inventors; and

(75) Inventors/Applicants (for US only): GUSTAFSSON, Bill [SE/SE]; Dragonvägen 8, S-444 41 Stenungsund (SE). OLSSON, Sune [SE/SE]; Stengodsvägen 3, S-444 95 Ödsmål (SE). FRIMAN, Bo [SE/SE]; Vårlöksvägen 13, S-444 45 Stenungsund (SE).

[FI/FI]; Keilaniemi, SF-02150 Espoo (FI).

(74) Agent: AWAPATENT AB; Box 5117, S-200 71 Malmö

(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, RU, SD, SE, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent), US.

Published

With international search report.

(54) Title: PROCESS FOR ELIMINATING ODOUR/TASTE-PRODUCING SUBSTANCES IN PLASTIC MATERIALS

(57) Abstract

A process for eliminating in plastic materials odour/taste-producing substances is described, the plastic material especially having the shape of water pipes, plastic containers or plastic film/sheeting for packing foodstuffs and pharmaceutical preparations, or interior fittings of plastic. In the process, there is added, during processing in the molten state, less than 0.5 wt.-%, preferably 0.05-0.3 wt.-%, of a substantially hydrophobic aluminium silicate molecular sieve having a pore diameter of at least 5.5 Å. ans Si/Al molar ratio in the crystal lattice of at least 35, preferably 200-500, and a sorption capacity for water at 25 °C and 4.6 torr of less-than 10 wt.-%, to the plastic material which subsequently is formed. The molecular sieve preferably has an average particle size not exceeding about 5 µm. The plastic material is a polyolefin plastic and is preferably selected among ethylene plastics and propylene plastics.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Austria	Fl	Finland	Ml	Mali
Australia	FR	France	MN	Mongolia
Barbados	GA	Ciabon	MR	Mauritania
Belgium	СB	United Kingdom	MW	Malawi
Burkina Faso	GN	Guinea	NL.	Netherlands
Bulgaria	GR	Greece	NO	Norway
Benin	HU	Hungary	PL	Poland
Brazil	IE	Ireland	RO	Romania
(*anada	IT	Haly	RU	Russian Federation
Central African Republic	JP	Japan	SD	Sudan
Congo	KP	Democratic People's Republic	SE	Sweden
Switzerland		of Korea	SN	Scnegal
Côte d'Ivoire	KK	Republic of Korea	SU	Soviet Union
Cameroon	Li	Liechtenstein	TD	Chad
Czechoslovakia	LK	Sri Lanka	TG	Togo
(jernany	LU	Luxembourg	us	United States of America
Denmark	MC	Monaco		
Spain	MG	Madagascar		
	Australia Barbados Belgium Burkina Faso Bulgaria Benin Brazil Canada Central African Republic Congo Switzerland Côte d'Ivoire Cameroon Czechoslovakia Germany Denmark	Australia FR Barbados GA Belgium GB Burkina Faso GN Bulgaria GR Benin HU Brazil IE Canada IT Central African Republic JP Congo KP Switzerfand Côte d'Ivoire KR Cameroon LI Czechoslovakia LK Giermany LU Denmark MC	Australia FR France Barbados GA Gabon Belgrum GB United Kingdom Burkina Faso GN Guinea Bulgaria GR Greece Benin HU Hungary Brazil IE Ireland Canada IT Italy Central African Republic JP Japan Congo KP Democratic People's Republic of Korea Căted d'Ivoire KR Republic of Korea Cameroon LI Liechtenstein Czechoslovakia LK Sri Lanka Germany LU Liecenbourg Denmark MC Monaco	Australia FR France MN Barbados GA Gabon MR Belgrum GB United Kingdom MW Burkina Faso GN Guinea NL Bulgaria GR Greece NO Benin HU Hungary PL Brazil IE Ireland RO C'anada IT Italy RU C'entral African Republic JP Japan SD C'ongo KP Democratic People's Republic SE Switzerland of Korea SN C'ôte d'Ivoire KR Republic of Korea SU C'ameroon LI Liechtenstein TD Czechoslovakia LK Sri Lanka TG Giermany LU Luxembourg US Denmark MC Monaco

15

1

PROCESS FOR ELIMINATING ODOUR/TASTE-PRODUCING SUBSTANCES IN PLASTIC MATERIALS

The present invention relates to a process for eli-5 minating odour/taste-producing substances in plastic materials. The invention particularly relates to the elimination of undesired, unintentionally added, odour/taste-producing substances from polyolefin type materials, by which are henceforth meant homopolymers of ethylene or propylene 10 or copolymers of one of these hydrocarbons with another alpha olefin, intended for fields of application where they may contact liquids or foodstuffs to be consumed by human beings or animals, or where any odour or taste may be experienced as negative for hygienic or aesthetic reasons.

In many contexts undesired, odour- and/or tasteproducing substances appear owing to chemical degradation or transformation in connection with production or compounding of plastic materials. These substances can be of 20 a highly varying chemical character. The occurrence ther of can constitute a health hazard or merely a source of irritation. Since the human being normally is most susceptible to odours and tastes, the substances need not appear in very high concentrations, but in most cases as 25 low concentrations as one or a few ppm are sufficient to make a taste or odour evident. To date, attempts have been made to overcome or at least reduce such odour and taste problems in various ways, such as by degassing the plastic material. Such a method is not only lengthy and expensive; 30 it also results in but a moderate improvement in respect of odour and taste, respectively.

Some specific fields will now be mentioned where the problem with undesired substances causing odour and/or taste is of particular significance.

35 Such a field comprises plastic pipes, more specifically plastic water pipes, where the emission of odourand/or taste-producing substances from the plastic material to the drinking water flowing through the pipe frequently is an annoying problem which is difficult to solve. The problem grows more serious by the fact that no details of the odour/taste-producing substance(s) are

5 known. It is believed that they consist of a variably composed mixture of different substances, such as oligomers, formed in the polymerisation, or volatile substances which have been formed by oxidisation processes in conjunction with subsequent steps of processing and which even at

10 further small concentrations of about 1-1000 ppm in the water give this an undesired odour and/or taste.

A second field comprises film and sheeting of plastic material, more particularly film and sheeting that is caused to contact foodstuffs and pharmaceutical preparations. Since for foodstuffs and pharmaceutical preparations extremely high requirements as regards purity are made and no foreign substances contaminating the foodstuff or pharmaceutical preparation are allowed for reasons of health and security, it is vital that plastic film and sheeting used for such products does not emit any undesired or contaminating substances. In such plastic products, there is also a particularly great risk that undesired substances are produced, such as when boiling the foodstuff in the wrapping, or when sterilising the drug packing by heat treatment or radiation.

A closely related field is represented by containers, such as bottles, of blow-moulded or moulded plastic, for packing foodstuffs, beverages or pharamceutical preparations.

A further field applies to interior fittings of plastic, e.g. panels, for use in buildings or cars and the like. In new cars, it thus is not unusual that the odour can be very unpleasant.

In all four fields mentioned above, the possible 35 odour which one may want to eliminate can appear especially in the compounding/processing of the plastic

material and in this context constitutes a problem in the working environment.

From a general point of view, it is known to remove any undesired odour and/or taste by means of adsorbing 5 substances, and as examples of such adsorbing substances, activated carbon, silica gel, activated aluminium oxide, diatomaceous earth and zeolites may be mentioned. An example in which a number of such additives are suggested, is Japanese Patent Specification JP 1,023,970 which thus is incorporated by reference. This publication suggests the adding of e.g. aluminium hydroxide, clay, diatomaceous earth, kaolin, talc, bentonite, activated carbon or activated carbon fibre for materials for packing foodstuffs to be heated in the packing. However, such additives have 15 been found to be without any appreciable effect, except under special circumstances, in the case of undesired components in plastic materials of the types concerned according to the present invention since, as a rule, they lose their absorbing capacity when contacting water or 20 water vapour.

Recently, US Patent Specification 4,795,482 has described a new type of zeolites intended for the elimination of undesired odour in certain contexts and supplied under one of the names ABSCENT or SMELLRITE. These zeo-25 lites are described to be crystalline, siliceous molecular sieves in which at least about 90, and preferably at least about 95, % of the tetrahedral oxide units of the crystal lattice are SiO, tetrahedra, and which have a sorption capacity for water at 25°C and 4.6 torr of less than 30 10 wt.-%. These zeolites have an Si/Al molar ratio of from 35 to infinity, preferably between 200 and 500, and a pore diameter of at least 5.5 Å, preferably at least 6.2 Å. It is also preferred that the sorption capacity for water vapour at 25°C and a water vapour pressure of 4.6 torr is 35 less than 6 wt.-%. These substantially hydrophobic molecular sieves are used to remove odorous organic compounds at a temperature of from -25°C to 100°C.

It should here be added that the above-mentioned Si/Al molar ratio for these molecular sieves applies to the oxide units of the crystal lattice only. The Si/Al molar ratio of the zeolite, which has been determined by conventional wet analysis, can be considerably lower owing to contamination by aluminous pollutants formed in the so-called dealuminification reaction which in many cases is included as a step in the production of the zeolite.

The above-mentioned zeolitic molecular sieves have proved useful above all for removing undesired odour from hygienic products, such as diapers, incontinence products and the like. Reference is here also made to EP 0,348,978.

As a further example of prior-art technique while using the same type of zeolite, US Patent 4,910,295 may be 15 mentioned. This patent relates to a specific process for reducing the odour of residual amounts of the comonomer ethylidene norbornene present in certain types of EPDM rubber.

One more example of prior art is US 4,826,497 concerning fibrous absorbent articles, such as diapers and
the like, intended for the absorption of body fluids. The
diaper contains a zeolite which can be loosely arranged
therein or, preferably, be immobilised.

According to the present invention, it has now sur25 prisingly been found that by adding the above type of
zeolitic molecular sieve it is possible to completely
eliminate the above problem with undesired, odour- and/or
taste-producing substances in plastic materials. By the
term plastic material is here meant polyolefin plastic.

30 The polyolefin plastic is preferably selected among ethylene plastic, i.e. plastic based on polyethylene or on
copolymers of ethylene, in which the ethylene monomer constitutes the largest part of the mass, or propylene plastic, i.e. plastic based on polypropylene or on copolymers

35 of propylene in which the propylene monomer constitutes

the largest part of the mass.

As indicated above, the invention concerns in a special aspect a process for eliminating, in plastic materials such as plastic pipes, plastic film and sheeting, plastic containers and plastic interior fittings, low contents of odour/taste-producing substances of unknown character, which have been formed by physical and/or chemical action in the polymerisation process or the subsquent compounding/processing.

More precisely, according to the invention it has

10 been found that the incorporation of small amounts of a
substantially hydrophobic aluminium silicate molecular
sieve, which preferably comprises a zeolite according to
the above-mentioned US Patent 4,795,482, permits simple
and more or less complete elimination of undesired odour
15 and/or taste-producing substances.

The characteristic features of the invention appear from the accompanying claims.

The invention is characterised in that it provides for a process for eliminating in plastic materials odourand/or taste-producing components which have been formed in polymerisation, heat treatment or radiation.

After a number of experiments, it has been found according to the invention that not all zeolites are active. Thus, it has been established that the zeolite should be substantially hydrophobic (oleophilic) to be effective in the elimination of odour and taste. A measure of the hydrophobic properties is the water sorption of the zeolite, and this should suitably be less than 10 wt.-%, preferably less than 6 wt.-%, at 25°C and 4.6 torr. The Si/Al molar ratio of the zeolite in the oxide units of its crystal lattice seems to affect the hydrophobic properties and should exceed 35 and preferably be between 200 and 500. The pore diameter of the zeolite, which according to the molecular size determines which compounds can be caught by the zeolite, should be at least 5.5 and preferably at least 6.2 Å.

WO 92/13029 PCT/SE92/00029

6

The zeolite, which generally is in the form of a powder, should have such a small particle size that it does not detrimentally affect the appearance of the plastic material or the other properties thereof. Thus, the zeolite should have an average particle size not exceeding about 10 μ m, such as about 0.1-7 μ m, preferably not exceeding about 5 μ m.

According to the invention, it has been found that a notably small amount of zeolite of less than 0.5 wt.-%, 10 preferably 0.05-0.3 wt.-%, is sufficient to eliminate any undesired odour and/or taste. This distinguishes from earlier applications in which zeolites have normally been used in considerably higher contents.

In the process according to the invention, the alumi-15 nium silicate molecular sieve (zeolite) is added to the plastic raw material which in its molten state should be compounded to pellets or finished material. The zeolite can be added either as it is or in the form of a so-called master batch, i.e. mixed with a polymer. In the extruder 20 or the corresponding compounding device, the components are mixed and the zeolite is uniformly distributed by dispersion in the molten polymer material. In the finished, formed plastic product, the zeolite will thus be present in this manner. It is surprising that, all the same, the zeolite can effectively produce its odour- and tasteeliminating effect, since it would have been assumed that the pores of the zeolite should be clogged by the molten plastic material. For some reason, however, this is not the case, but the zeolite can effectively catch and elimi-30 nate undesired, odour- and/or taste-causing substances.

For further elucidation of the invention an Example follows below.

EXAMPLE

For the purpose of determining the emission of taste- '
35 causing substances from different plastic materials, a
great number of materials have been tested while using a
taste panel. The testing materials have been produced by

compounding an HD polyethylene having a density of 945 kg/m³ and containing normal additives that are required for stabilisation/ processing and also serving as reference material, and different molecular sieve materials at 220°C, on the one hand in a laboratory Buss-Kneter and, on the other hand, in a full-scale production line. The material was pelleted in conjunction with the extrusion. From pellets, a sample of 32 g was taken for each test, which was stirred for 4 h at a temperature of 30 ± 1°C by a magnetic agitating means in a flask fitted with a groundin plug and containing 1000 ml of pure distilled water. Five sub-samples were then prepared from each sample by dilution according to the Table below.

TABLE 15 Sub-sample Sample water Dilution water Taste/odour level No. ml ml degree 1.5

The level of taste and odour is here defined as follows: (a + b)/a wherein a is the amount of sample water in
the sub-sample in which odour or taste is barely detectable, while b is the amount of dilution water in the same
sub-sample. The lower the value of the taste and odour
level the better the result. A value of 1.5 and below is
acceptable. Seven trained taste testers are allowed to
estimate each sample and determine their personal taste
level. The average value of the seven people is considered
to produce an objective estimation thereof. The testing
is blind, i.e. the taste panel cannot distinguish the
sampl s.

A total of 14 samples were examined according to this procedure, and the results were as follows:

PCT/SE92/00029

8 TABLE 2

			1000	<u></u>					
Sample	Addi-	Con-	Pro-	Pa	anel	Est:	imate	9	Taste
	tive	tent	cess-	St	ub-s	ample	e No	•	Level
		wt8	ing	1	2	3	4	5	
									
1			P	7	7	6	6	5	>8
2	•		P	6	6	6	6	5	>8
3	EA.	0.22	P	7	7	7	7	6	>8
4	A3	0.22	P	6	6	6	5	3	4-8
5	A3	0.22	P	7	7	7	6	1	4-8
6	A10	0.12	P	7	7	· 6	6	4	>8
7	A10	0.11	P	7	7	7	7	6	>8
8	A10	0.10	P	7	7	7	6	4	>8
9	ABSC	0.27	P	2	1	1	0	0	<1
10	ABSC	0.27	P	5	3	2	1	0	1-1.5
11	ABSC	0.28	P	3	2	1	0	0	<1
12	ABSC	0.25	В	0	0	0	0	0	<1
13	ABSC	0.10	В .	0	0	0	0	0	<1
14	ABSC	0.05	В	0	0	0	0	0	<1
	1 2 3 4 5 6 7 8 9 10 11 12	1 2 3 A3 4 A3 5 A3 6 A10 7 A10 8 A10 9 ABSC 10 ABSC 11 ABSC 11 ABSC 12 ABSC 13 ABSC	tive tent wt% A3 0.22 A3 0.22 A4 A3 0.22 5 A3 0.22 6 A10 0.12 7 A10 0.11 8 A10 0.10 9 ABSC 0.27 10 ABSC 0.27 11 ABSC 0.28 12 ABSC 0.25 13 ABSC 0.10	Sample Addi- Con- Pro- tive tent cess- wt% ing P P AMMINISTRICT	Sample Addi- Con- Pro- Pro- Pro- tive tent cess- Start wt% ing 1 1	Sample Addi- Con- Pro- Panel tive tent cess- Sub-sample wt% ing 1 2 1	Sample Addi- Con- Pro- Panel Estrictive tent cess- Sub-sample wt% ing 1 2 3 1 P 7 7 6 2 P 6 6 6 6 3 A3 0.22 P 7 7 7 7 4 A3 0.22 P 6 6 6 6 5 A3 0.22 P 7 7 7 7 6 A10 0.12 P 7 7 6 7 A10 0.11 P 7 7 7 7 8 A10 0.10 P 7 7 7 7 9 ABSC 0.27 P 2 1 1 10 ABSC 0.27 P 5 3 2 11 ABSC 0.28 P 3 2 1 12 ABSC 0.25 B 0 0 0 13 ABSC 0.10 B 0 0 0	Sample Addi- tive tent cess- Sub-sample No wt% ing 1 2 3 4 1 P 7 7 6 6 2 P 6 6 6 6 3 A3 0.22 P 7 7 7 4 A3 0.22 P 6 6 6 5 5 A3 0.22 P 7 7 7 6 6 A10 0.12 P 7 7 6 6 7 A10 0.11 P 7 7 7 6 9 ABSC 0.27 P 2 1 1 0 10 ABSC 0.27 P 5 3 2 1 11 ABSC 0.28 P 3 2 1 0 12 ABSC 0.25 B 0 0 0 0 13 ABSC 0.10 B 0 0 0 0	Sample Addi- tive tent cess- Sub-sample No. wt% ing 1 2 3 4 5 1 P 7 7 6 6 5 2 P 6 6 6 6 5 3 A3 0.22 P 7 7 7 7 6 4 A3 0.22 P 6 6 6 5 3 5 A3 0.22 P 7 7 7 6 1 6 A10 0.12 P 7 7 6 4 7 A10 0.11 P 7 7 7 6 8 A10 0.10 P 7 7 7 6 4 9 ABSC 0.27 P 2 1 1 0 0 10 ABSC 0.28 P 3 2 1 0 0 12 ABSC 0.25 B 0 0 0 0 0 13 ABSC 0.10 B

20

A3 and A10 are common, non-hydrophobic zeolites which are supplied by Grace GmbH under the tradename "Sylosiv 3A" and "Sylosiv 10A", respectively. ABSC stands for ABSCENT which is the tradename of a zeolite produced according to 25 US Patent 4,795,482. "P" implies that the sample has been run on a production scale in a compounding line, whereas "B" implies that the sample has been run on a laboratory scale in a small Buss-Cokneter. The figures under the heading "Panel Estimate" state how many of the people in 30 the taste panel which have noticed the taste in the subsample 1, 2, 3, 4 and 5 of the respective main sample. Table 2 shows that the adding of conventional zeolite (Samples 3-8) produces no effect or a very poor effect in respect of eliminating odour/taste-causing substances,

35 whereas the adding of a zeolite according to the invention (Samples 9-14) gives an excellent result.

9

CLAIMS

- Process for eliminating in plastic materials
 odour/taste-producing substances, c h a r a c t e r i s e d in that the plastic material is selected among
 ethylene plastics or propylene plastics, and that to said
 plastic material, during processing in the molten state,
 there is added less than 0.5 wt.-% of a substantially
 hydrophobic aluminium silicate molecular sieve having a
 pore diameter of at least 5.5 Å, an Si/Al molar ratio in
 the crystal lattice of at least 35, and a sorption capacity for water at 25°C and 4.6 torr of less than 10 wt.-%.
- 2. Process as claimed in claim 1, c h a r a c
 15 t e r i s e d in that the molecular sieve added has an

 Si/Al molar ratio in the crystal lattice of between 200

 and 500, and that it has a sorption capacity for water at

 25°C and 4.6 torr of less than 6 wt.-%.
- 3. Process as claimed in any one of the preceding 20 claims, c h a r a c t e r i s e d in that the molecular sieve added has an average particle size not exceeding 5 µm.
- 4. Process as claimed in any one of the preceding claims, character is ed in that the molecular sieve is added in an amount of 0.05-0.3 wt.-%.
- 5. Process for eliminating, in pipes, preferably water pipes, of ethylene plastic or propylene plastic, the emission of odour/taste-producing substances, c h a r a c t e r i s e d in that less than 0.5 wt.-%, preferably 0.05-0.3 wt.-%, of a substantially hydrophobic aluminium silicate molecular sieve having an Si/Al molar ratio in the crystal lattice above 35, preferably 200-500, a pore diameter of at least 5.5 Å and a sorption capacity for water at 25°C and 4.6 torr of 1 ss than 10 wt.-%, is added to the plastic material, and that this is subsequently formed to a pipe.

- 6. Process for eliminating, in film or sheeting, preferably for packing foodstuffs or pharmaceutical preparations, of ethylene plastic or propylene plastic, the emission of odour- and/or taste-producing substances,
- 5 characterised in that less than 0.5 wt.-%, preferably 0.05-0.3 wt.-%, of a substantially hydrophobic aluminium silicate molecular sieve having an Si/Al molar ratio in the crystal lattice above 35, preferably 200-500, a pore diameter of at least 5.5 Å and a sorption capacity for water at 25°C and 4.6 torr of less than 10 wt.-%, is added to the plastic material, and that this is subsequently formed to a film or sheeting.
- 7. Process for eliminating, in blow-moulded or moulded plastic bottles or containers of ethylene plastic or propylene plastic, the emission of odour/taste-producing substances, c h a r a c t e r i s e d in that less than 0.5 wt.-%, preferably 0.05-0.3 wt.-%, of a substantially hydrophobic aluminium silicate molecular sieve having an Si/Al molar ratio in the crystal lattice above 35, preferably 200-500, a pore diameter of at least 5.5 Å and a sorption capacity for water at 25°C and 4.6 torr of less than 10 wt.-%, is added to the plastic material, and that this is subsequently formed to a bottle or container.
- 8. Process for eliminating, in interior fittings,

 25 preferably for use in buildings or cars, of ethylene plastic or propylene plastic, the emission of odour-producing substances, c h a r a c t e r i s e d in that less than 0.5 wt.-%, preferably 0.05-0.3 wt.-%, of a substantially hydrophobic aluminium silicate molecular sieve having an 30 Si/Al molar ratio in the crystal lattice above 35, preferably 200-500, a pore diameter of at least 5.5 Å and a sorption capacity for water at 25°C and 4.6 torr of less than 10 wt.-%, is added to the plastic material, and that this is subsequently formed to the interior fitting 35 desired.

International Application No PCT/SE 92/00029

	ION OF SUBJECT MATTER (if several classi				
	rnational Palent Classification (IPC) or to both I K 3/34, C 08 L 23/00	National Classification and IPC			
II. FIELDS SEAR	CHED				
	Minimum Docume	entation Searched			
Classification System Classification Symbols					
IPC5	C 08 K; C 08 L				
		r than Minimum Documentation ts are Included in Fields Searched ⁸			
SE,DK,FI,NO	classes as above				
III. DOCUMENTS	CONSIDERED TO BE RELEVANT9		****		
Category Ci	tation of Document,11 with Indication, where ap	propriate, of the relevant passages 12	Relevant to Claim No.13		
	A, 4795482 (GIOFFRE ET AL)		1-8		
	see the whole document	3 danuary 1365,	1.0		
	A, 4826497 (MARCUS ET AL) 2 see the whole document 	May 1989,	1-8		
	A, 4855154 (GIOFFRE ET AL) see the whole document	8 August 1989,	1-8		
	A, 4910295 (BERNIER ET AL) see the whole document	20 March 1990,	1-8		
	A, 5013335 (MARCUS) 7 May 1 see the whole document 	991,	1-8		
1.	يب فته ري بي فت لين				
}					
"A" document d considered	* Special categories of cited documents: 10 "A" document defining the general state of the art which is not considered to be of particular relevance "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention				
"E" earlier docu filing date	ment but published on or after the international	"X" document of particular relevance cannot be considered novel or c	e, the claimed invention annot be considered to		
"L" document w which is cit	hich may throw doubts on priority claim(s) or ed to establish the publication date of another	involve an inventive step			
"O" document re other means	citation of other special reason (as specified) comment referring to an oral disclosure, use, exhibition or other means comment referring to an oral disclosure, use, exhibition or other means considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.				
"P" document p	ublished prior to the international filing date bu ne priority date claimed	* "&" document member of the same	patent family		
IV. CERTIFICATION					
Date of the Actual (Completion of the International Search	Date of Mailing of this International Se	earch Report		
International Searc	hing Authority	Signature of Authorized Officer	J.		
	EDISH PATENT OFFICE (econd sheet) (January 1985)	Jack Hedlund	~~		

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 92/00029

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 28/02/92 The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document	Publication	Patent family	Publication
cited in search report	date	member(s)	date

	Patent document cited in search report	Publication date	Patei me	Publication date	
US-A- 4795482		89-01-03	AU-B-		602411
			AU-D-	1854288	89-01-05
			EP-A-	0297543	89-01-04
		•	JP-A-	1085113	89-03-30
			US-A-	4826497	89-05-02
			US-A-	4855154	89-08-08
			US-A-	5013335	91-05-07
US-A-	4826497	89-05-02	AU-B-	602411	90-10-11
		AU-D-	1854288	89-01-05	
			EP-A-	0297543	89-01-04
		JP-A-	1085113	89-03-30	
		US-A-	4795482	89-01-03	
		US-A-	4855154	89-08-08	
			US-A-	5013335	91-05-07
			JP-A-	2006659	90-01-10
US-A-	4855154	89-08-08	AU-B-	602411	90-10-11
			AU-D-	1854288	89-01-05
			EP-A-	0297543	89-01-04
			JP-A-	1085113	89-03-30
			US-A-	4795482	89-01-03
			US-A-	4826497	89-05 -0 2
			US-A-	5013335	91-05-07
US-A- 4910295	90-03-20	CA-A-	2015628	90-10-28	
			EP-A-	0395104	90-10-31
~~			JP-A-	2302404	90-12-14
US-A-	5013335	91-05-07	AU-B-	602411	90-10-11
· ·			AU-D-	1854288	89-01-05
			EP-A-	0297543	89-01-04
			EP-A- JP-A-	1085113	89-01-04 89-03-30
			JP-A- US-A-	1085113 4795482	
			JP-A-	1085113	89-03-30